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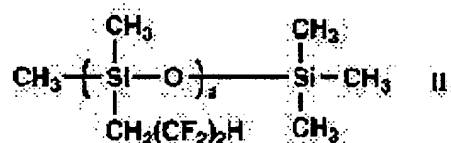
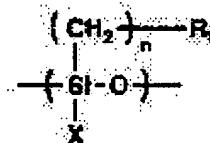
(54) THERMAL FIXING METHOD

(57)Abstract:

PROBLEM TO BE SOLVED: To improve offset resistance and OHP transmissivity by using fluorine-contained silicone oil provided with a specified structure unit, and also specifying the storage elastic modulus and loss elastic modulus of toner.

SOLUTION: The fluorine-contained silicone oil having the structure unit shown by an expression is used, and also, the storage elastic modulus G'160 of the toner constituted of resin and coloring agent is 500 to 1200dyn/cm² at 160°C, the loss elastic modulus G''160 is 1500 to 3000dyn/cm², at 160°C, the storage elastic modulus G'180 is 300 to 1000dyn/cm², at 180°C and the loss elastic modulus G''180 is 800 to 2300dyn/cm² at 180°C. In the expression, X denotes a saturated

hydrocarbons group of 1 to 4C, or an aryl group, R1 denotes a fluoro alkyl group of 2 to 10C, and (n) denotes integer 1 to 4.



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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the heat fixing approach of fixing a toner image to record material.

[0002]

[Description of the Prior Art] Conventionally, the thermal efficiency of the toner image supported on record material in the xerography is good, and the object for prizes of the heat roller fixing approach has been carried out from reasons suitable for high-speed fixing. This heat roller fixing approach is an approach of passing the recording paper which supported the toner image for between the fixing rollers and sticking-by-pressure rollers which contained the source of heating, and carrying out thermofusion fixing of the toner to the recording paper.

[0003] While this heat roller fixing approach has the above-mentioned advantage, the toner in the record paper adheres to a transfer paper at a fixing roller, and adheres to other parts of the recording paper after rotation, it is fixed to it, and it has the demerit which soils the image of the obtained recording paper in which the so-called offset phenomenon occurs.

[0004] The technique which supplies a dimethyl silicone oil to a fixing roller front face conventionally is proposed for offset-phenomenon prevention of the heat roller fixing approach.

[0005] Although this approach was effective in prevention of an offset phenomenon, it needed the equipment for opposite side silicone oil supply, and had the problem of emitting smoke. Furthermore, the smooth nature of a fixing image front face is spoiled by spreading of a silicone oil, and when it is especially a color picture, the fall of OHP permeability is caused.

[0006] Although it demonstrates the outstanding effectiveness for prevention of an offset phenomenon to be sure, the technique by which the proposal is made [above-mentioned] had the problem of fixable fully being unable to demonstrate, and for this reason, the blemish of a fixing roller occurs, or its life of a fixing roller is short and it has raised problems -- the image stabilized over the long period of time cannot be obtained. Moreover, a silicone oil is forward electrification nature as frictional electrification nature conventionally, and it is easy to carry out forward electrification of the fixing roller front face. For this reason, when it was easy to produce the phenomenon in which the recording paper coils around a fixing roller when the toner of negative electrification nature is used and the conventional silicone oil was used for a fixing roller, use of a toner had constraint. This produced the problem that dust and Chile adhere to a fixing roller, a blemish occurs in a fixing roller like the above, and continued at a long period of time and an image defect occurred.

[0007] A pressure welding is carried out to a sticking-by-pressure roller through the film material which moves on the other hand using the heating object fixed instead of the fixing roller in recent years, the recording paper which supported the toner image for the meantime is passed, and the technique which carries out heat fixing is proposed by JP,5-119530,A.

[0008] Although this fixing approach is the good fixing approach of thermal efficiency, it has raised many of the same problems as the heat roller fixing approach mentioned above.

[0009]

[Problem(s) to be Solved by the Invention] The purpose of this invention has offset-proof nature in offering the heat fixing approach using the good toner for electrostatic-charge development with good OHP permeability.

[0010]

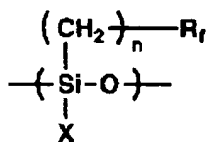
[Means for Solving the Problem] The above-mentioned purpose of this invention is attained by the following configurations.

[0011] 1. In Heat Fixing Approach of Passing Record Material Which Supported Toner Image for between Sticking-by-Pressure Rollers Which Carry Out Pressure Welding to Rotating Fixing Roller in Which Silicone Oil Paint Film was Formed on Front Face, and this Fixing Roller, and Fixing this Toner Image to Record Material It is the ***** silicone oil in which this silicone oil has the structural unit shown by the following general formula [I]. And 160 is 1500 - 3000 dyn/cm² the loss modulus [in / in the storage modulus G'160 in 160 degrees C of this toner that consists of resin and a coloring agent at least / 500 - 1200 dyn/cm², 160 degree C] of G." The heat fixing approach characterized by being the toner for electrostatic-charge development whose storage modulus G'180 in 180 degrees C is 300 - 1000 dyn/cm², and whose 180 is 800 - 2300 dyn/cm² the loss modulus of G" in 180 degrees C.

[0012]

[Formula 2]

一般式 [I]



[0013] (X shows the saturated hydrocarbon radical or aryl group of carbon numbers 1-4 among a [general formula I] type, R_f shows the fluoro alkyl group of carbon numbers 2-10, and n shows the integer of 1-4.)

2. In Heat Fixing Approach of Passing Record Material Which Supported Toner Image for between Sticking-by-Pressure Rollers Which Carry Out Pressure Welding to Rotating Fixing Roller in Which Silicone Oil Paint Film was Formed on Front Face, and this Fixing Roller, and Fixing this Toner Image to Record Material It is the ***** silicone oil in which this silicone oil has the structural unit shown by said general formula [I]. More than molecular weight 01500 of the tetrahydrofuran (THF) dissolution component of this toner that consists of resin and a coloring agent at least The heat fixing approach characterized by being the toner for electrostatic-charge development whose ratios (SLp/SHp) of the area (SLp) of less than 80,000 low molecular weight constituent and the area (SHp) of the amount component of macromolecules of molecular weight 80,000-1 million are 5-15.

[0014] Hereafter, this invention is further stated to a detail.

[0015] The ***** silicone oil of this invention is a silicone oil which has the structural unit shown by said general formula [I].

[0016] In a general formula [I], X shows aryl groups, such as a saturated hydrocarbon radical of the alkyl group of the carbon numbers 1-4, such as a methyl group, and a phenyl group, and R_f is the fluoro alkyl group of carbon numbers 2-10.

[0017] furthermore, it is the radical expressed with Z-(CF₂)_m- (Z -- a hydrogen atom or a fluorine atom, and m -- like the above-mentioned fluoro alkyl group -- 2-10 -- it is the integer of 2-8 preferably.) as a desirable mode of R_f, and n expresses the integer of 1-4.

[0018] Although the ***** silicone oil of this invention needs to have the above-mentioned repeat unit, you may have copolymer structure with dimethyl silicon, phenylmethyl silicon, or diphenyl silicon.

[0019] As for the ***** silicone oil in this invention, it is desirable that it is the liquefied thing which has moderate viscosity at the time of use. For this reason, in the silicone oil of this invention, the

viscosity in 25 degrees C has desirable 20-1000cs, and what has the viscosity of 100-500cs more preferably is good.

[0020] Adjustment of the viscosity of the above-mentioned ***** silicone oil is controllable by adjusting polymerization degree. This viscosity shows dynamic viscosity and is ASTM. D 445-46T or JIS It is measured by the Ubbelohde viscometer based on Z8803.

[0021] the structural unit shown by the general formula [I] of this invention from whenever [many purpose achievement / of this invention] when the ***** silicone oil of this invention is a copolymer -- more than 20mole% -- being contained is desirable. The effectiveness of a fluorine system silicone oil will not be demonstrated as it is less than [20mole%], but the effectiveness of other components will be demonstrated notably.

[0022] hydrolyzing the compound which the manufacture approach of the fluorine system silicone oil of this invention referred to the manufacture approach of the usual silicone oil, and silicon and chlorination alkyl were made to react and was obtained in dialkyl permutation dichlorosilane -- a siloxane and nothing -- subsequently -- annular oligomer or a line -- after forming oligomer, it is compounded by carrying out the polymerization of these.

[0023] Although the fluorine system silicone oil compound of this invention has alkyl group fluoride in the side chain, it is manufactured easily instead of chlorination alkyl in this case by using the thing of the structure shown with the fluorine system compound which has a chloro radical at the end, for example, the following general formula, (b).

[0024] General formula (b)

In a Z-(CF₂)_m(CH₂)_nCl general formula (b), m shows the integer of 2-10 and n shows the integer of 1-4. Moreover, Z shows hydrogen or a fluorine element.

[0025] The typical concrete target of the compound shown by the general formula (b) is listed to below.

[0026] (A)CF₃CF₂CH₂Cl (B)CF₃CF₂CF₂CH₂Cl (C)CF₃CF₂CF₂(CH₂)₂Cl (D)CF₃CF₂CF₂CF₂

(CH₂)₂Cl (E)CF₃CF₂CF₂CF₂CH₂Cl (F)CF₃CF₂CF₂CF₂CF₂ (CH₂)₃Cl (G)

CF₃CF₂CF₂CF₂CF₂CH₂Cl (H)CF₃CF₂CF₂CF₂CF₂CF₂CH₂Cl (I)HCF₂CF₂CH₂Cl (J)

HCF₂CF₂CF₂CH₂Cl (K)HCF₂CF₂CF₂(CH₂)₂Cl (L)HCF₂CF₂CF₂CF₂CH₂Cl (M) --

HCF2CF2CF2CF2(CH2)2Cl(N) HCF2CF2CF2CF2 (CH2) -- 4Cl(O) HCF2CF2CF2CF2CF2 (CH2) --

3Cl(P) HCF₂CF₂CF₂CF₂CF₂ -- in addition 2 Cl 2 CH 2 CF As chlorination alkyl which introduces alkyl groups other than alkyl group fluoride in this invention, a methyl chloride, an ethyl chloride, a propyl chloride, and a butyl chloride can be raised.

[0027] In this invention, in order to demonstrate effectiveness, such as homogeneity adhesion to the fixing roller by which fluorine system resin covering was carried out by using the silicone oil by which fluorination alkylation was carried out [above-mentioned], this fluorine atomic number is presumed to be what has done the big role so.

[0028] In this case, the carbon numbers of fluorination alkyl are 1-10, and, as for the part coupled directly with a silicon atom, it is desirable that it is a methylene chain. Furthermore, the carbon number range of suitable fluorination alkyl is 2-8. When this fluorination alkyl carbon number became excessive and heat is added, a problem is produced in the flowability of a fixing roller. Moreover, in not having fluorination alkyl, there is no wettability improvement to the hot calender roll front face which covered fluorine system resin, and formation of the uniform oil film cannot be performed.

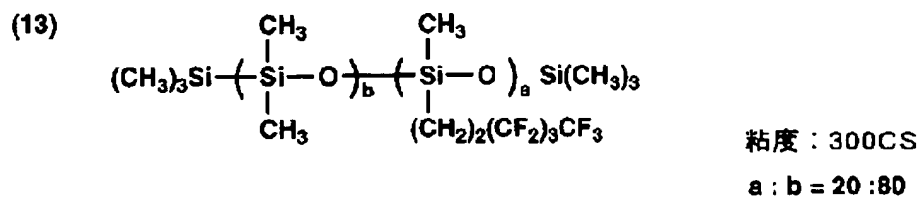
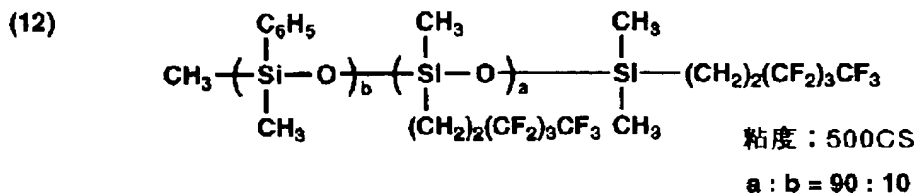
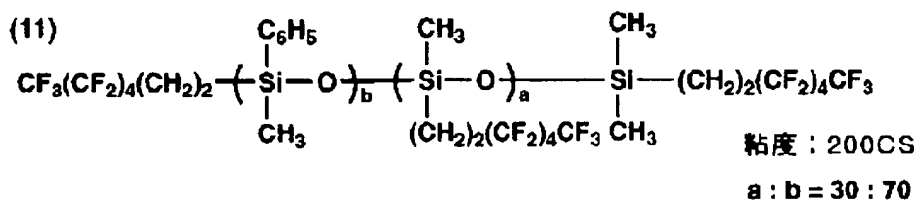
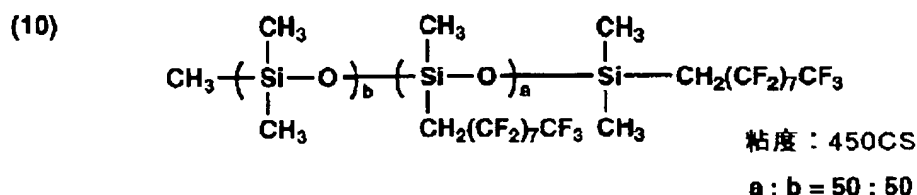
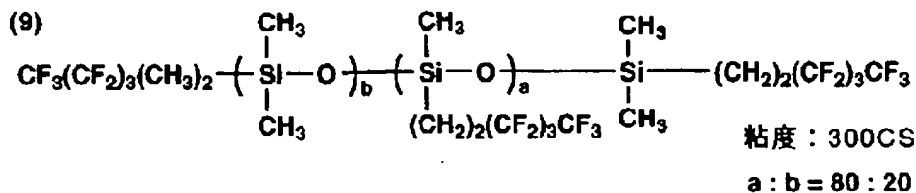
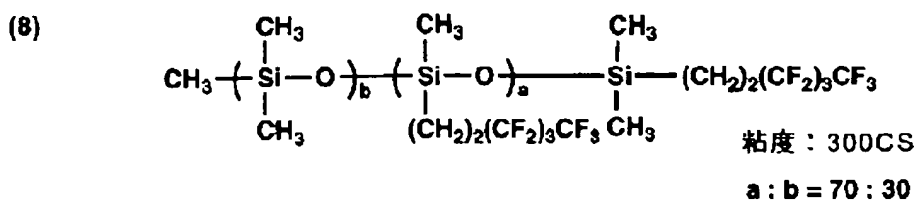
[0029] The structure of the typical example of the ***** silicone oil of this invention is shown below.

[0030]

[Formula 3]

- (1)
$$\text{CH}_3 - \left(\begin{array}{c} \text{CH}_3 \\ | \\ \text{Si} - \text{O} \\ | \\ \text{CH}_2(\text{CF}_2)_2\text{H} \end{array} \right)_a - \begin{array}{c} \text{CH}_3 \\ | \\ \text{Si} - \text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$$
 粘度 : 450CS
- (2)
$$\text{CH}_3 - \left(\begin{array}{c} \text{CH}_3 \\ | \\ \text{Si} - \text{O} \\ | \\ (\text{CH}_2)_2(\text{CF}_2)_2\text{CF}_3 \end{array} \right)_a - \begin{array}{c} \text{CH}_3 \\ | \\ \text{Si} - \text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$$
 粘度 : 250CS
- (3)
$$\text{CH}_3 - \left(\begin{array}{c} \text{CH}_3 \\ | \\ \text{Si} - \text{O} \\ | \\ (\text{CH}_2)_2(\text{CF}_2)_3\text{CF}_3 \end{array} \right)_a - \begin{array}{c} \text{CH}_3 \\ | \\ \text{Si} - \text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$$
 粘度 : 300CS
- (4)
$$\text{CH}_3 - \left(\begin{array}{c} \text{CH}_3 \\ | \\ \text{Si} - \text{O} \\ | \\ \text{CH}_2(\text{CF}_2)_6\text{CF}_3 \end{array} \right)_a - \begin{array}{c} \text{CH}_3 \\ | \\ \text{Si} - \text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$$
 粘度 : 500CS
- (5)
$$\text{CH}_3 - \left(\begin{array}{c} \text{CH}_3 \\ | \\ \text{Si} - \text{O} \\ | \\ (\text{CH}_2)_2(\text{CF}_2)_4\text{CF}_3 \end{array} \right)_a - \begin{array}{c} \text{CH}_3 \\ | \\ \text{Si} - \text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$$
 粘度 : 350CS
- (6)
$$\text{CH}_3 - \left(\begin{array}{c} \text{CH}_3 \\ | \\ \text{Si} - \text{O} \\ | \\ \text{CH}_3 \end{array} \right)_b - \left(\begin{array}{c} \text{CH}_3 \\ | \\ \text{Si} - \text{O} \\ | \\ \text{CH}_2(\text{CF}_2)_2\text{CF}_3 \end{array} \right)_a - \begin{array}{c} \text{CH}_3 \\ | \\ \text{Si} - \text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$$
 粘度 : 320CS
a : b = 80 : 20
- (7)
$$\text{CH}_3 - \left(\begin{array}{c} \text{CH}_3 \\ | \\ \text{Si} - \text{O} \\ | \\ \text{CH}_3 \end{array} \right)_b - \left(\begin{array}{c} \text{CH}_3 \\ | \\ \text{Si} - \text{O} \\ | \\ (\text{CH}_2)_2(\text{CF}_2)_3\text{CF}_3 \end{array} \right)_a - \begin{array}{c} \text{CH}_3 \\ | \\ \text{Si} - \text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$$
 粘度 : 300CS
a : b = 60 : 40

[0031]



[Formula 4]

[0032] In addition, in the above-mentioned compound, a and b show one or more integers, are the integer of 10-2000 preferably, and are 100-1000 more preferably.

[0033] Next, the toner for electrostatic-charge development of this invention (only henceforth the toner of this invention) is explained in full detail.

[0034] <GPC measuring method> The molecular weight distribution of the resin in this invention are measured by the molecular weight distribution of the chromatogram by GPC which used the tetrahydrofuran (THF) extractives and THF of a toner as the solvent, and measurement is the following

conditions. A test portion is the following, and is made and created.

[0035] After mixing a sample and THF by the concentration of 0.5-5mg (for example, 5mg/(ml))/ml and carrying out neglect at a room temperature for several hours (for example, 5 - 6 hours), it fully shakes, and it mixes with THF well (until the coalescence object of a sample is lost), and gentle placement is further carried out at a room temperature for 12 hours or more (for example, 24 hours). It is made for the time amount of the mixing point in time of a sample and THF to a standing termination time to turn into 24 hours or more (for example, 24 - 30 hours) at this time.

[0036] Then, let what passed the sample processing filter (pore size, 0.45-0.5 micrometers, for example, my SHORI disk H-25-5 TOSOH CORP. make, made in EKI KURO disk 25CR germane Science Japan, etc. can be used) be the sample of GPC. Sample concentration is adjusted so that a toner component may become in ml and 0.5-5mg /.

[0037] In a GPC measuring device, in a 40-degree C heat chamber, a column is stabilized, as a solvent, 100microl impregnation of a sink and the THF sample solution is carried out, and THF is measured by the rate of flow 1ml/m in the column in this temperature. In the molecular weight measurement of a sample, the molecular weight distribution which a sample has is computed from the relation of the opposite numeric value of a calibration curve and the number of counts which were created by several sorts of mono dispersion polystyrene standard samples.

[0038] It is appropriate to use the standard polystyrene sample of about at least ten points as a standard polystyrene sample for calibration-curve creation, for example using the TOSOH CORP. make or the thing whose molecular weight by Showa Denko K.K. is 102 to about 107. RI (refractive index) detector is used for a detector. As a column, are good to combine two or more commercial polystyrene gel columns. For example, shodex by Showa Denko K.K. GPC The combination of KF-801, and 802, 803, 804 and 805, 806, 807, 800P, TSKgelG1000H (HXL) by TOSOH CORP., G2000H (HXL), G3000H (HXL), G4000H (HXL), G5000H (HXL), G6000H (HXL), G7000H (HXL), TSK The combination of guardcolumn can be mentioned.

[0039] a <viscoelasticity measuring method> -- storage-modulus G' and the loss modulus of G'' -- a rheometer -- " -- soliquid meter: -- the value (dyne/cm²) measured by the cone plate method using MR-500 mold" (Japanese rheology company make) shall be said here -- as a Measuring condition -- a cone angle -- 2.0deg(s) and the diameter of a cone -- 50 micrometers and measurement initiation temperature were made into 100 degrees C, and the programming rate was made [4.0cm and a frequency / 1.0Hz and an angle of torsion] into 3 degrees C/m for 0.5deg(s) and gap length.

[0040] G'' of loss moduli [in / for the storage modulus in 160 degrees C / G'_{160} and 160 degrees C] is set to 160, and G'' of loss moduli [in / for the storage modulus in 180 degrees C / G'_{180} and 180 degrees C] is set to 180.

[0041] this invention -- setting -- at least -- resin -- and -- a coloring agent -- from -- becoming -- a toner -- 160 -- degree C -- it can set -- a storage modulus -- $G' -- ' -- 160 -- 500 - 1200 -- dyn/cm -- 2,160 -- degree C -- it can set -- a loss modulus -- $G'' -- " -- 160 -- 1500 - 3000 -- dyn/cm -- two -- it is -- 180 -- degree C -- it can set -- a storage modulus -- $G' -- ' -- 180 -- 300 - 1000 -- dyn/cm -- two -- it is -- 180 -- degree C -- it can set -- a loss modulus -- $G'' -- " -- 180 -- 800 - 2300 -- dyn/cm -- two -- it is -- electrostatic charge -- development -- ** -- a toner -- using it .$$$$

[0042] Moreover, it is required $G'_{160} > G'_{180}$ and for $160 > G'$ to G' be 180.

[0043] If the storage modulus G'_{160} of the toner in 160 degrees C exceeds 1200 dyn/cm² in this invention and 160 exceeds 3000 dyn/cm² the loss modulus of G'' in 160 degrees C, the smooth nature on the front face of an image runs short, and OHP permeability causes the fall of saturation low as an image.

[0044] On the other hand, although the smooth nature on the front face of an image is good in the storage modulus G'_{160} in 160 degrees C being less than 500, and 160 being less than 1500 the loss modulus of G'' in 160 degrees C, it is easy to generate problems, such as offset.

[0045] Moreover, if the storage modulus G'_{180} in 180 degrees C exceeds 1000 dyn/cm² and 180 exceeds 2300 dyn/cm² the loss modulus of G'' in 180 degrees C, the wettability to imprint material and an adhesive property will become low, and will tend to produce the problem of a fixing undershirt etc.

[0046] It is easy to generate problems, such as offset, like what was mentioned above on the other hand as the storage moduli $G'180$ in 180 degrees C are less than two 300 dyn/cm and 180 is less than two 800 dyn/cm the loss modulus of G'' in 180 degrees C.

[0047] Furthermore, it is desirable in order that it may stabilize OHP permeability $G'160 > G'180$ and that $160 > G''$ is $[G'']$ 180.

[0048] In the chromatogram measured by the gel permeation chromatography (GPC) of said toner, the ratios (SLp/SHp) of the area (SLp) of less than 80,000 low molecular weight constituent and the area (SHp) of the amount component of macromolecules of molecular weight 80,000-1 million of the toner of this invention are 5-15 more than molecular weight 01500. In this case, it is difficult to obtain a penetrable good OHP image in heat roller fixing as SLp/SHp is less than five. Moreover, if SLp/SHp exceeds 15, it will become difficult to keep hot-proof offset nature good.

[0049] In order to acquire basic properties as a toner, such as an electrification property and a grindability, as for the vinyl system binding resin which can be used for this invention, it is desirable to make a styrene system monomer, acrylic ester, or a methacrylic ester monomer into a base unit.

[0050] As an example of the above-mentioned styrene monomer, o-methyl styrene, p-methyl styrene, alpha-methyl-styrene, p-ethyl styrene, 2, 4-dimethyl styrene, p-n-butyl styrene, p-ter-butyl styrene, p-n-hexyl styrene, p-n-octyl styrene, p-n-dodecyl styrene, p-methoxy styrene, p-phenyl styrene, P-chloro styrene, 3, and 4-dichloro styrene etc. is mentioned other than styrene.

[0051] As an example of the acrylic ester or the methacrylic ester monomer used for this invention A methyl acrylate, an ethyl acrylate, acrylic-acid propyl, acrylic-acid n-butyl, Isobutyl acrylate, acrylic-acid n-octyl, methacrylic-acid dodecyl, 2-ethylhexyl methacrylate, acrylic-acid stearyl, a methyl methacrylate, Ethyl methacrylate, methacrylic-acid propyl, n-butyl methacrylate, Methacrylic-acid isobutyl, n-octyl methacrylate, methacrylic-acid dodecyl, Others [ester / acrylic acids, such as stearyl methacrylate, or / methacrylic / alkyl], Acrylic-acid 2-chloro ethyl, acrylic-acid phenyl, alpha-chloro methyl acrylate, Methacrylic-acid phenyl, dimethylaminoethyl methacrylate, diethylaminoethyl methacrylate, Methacrylic-acid 2-hydroxyethyl, methacrylic-acid GURISHIJIN, bis-glycidyl methacrylate, Polyethylene glycol dimethacrylate, methacryloxyethyl phosphate, etc. can be mentioned. An ethyl acrylate, acrylic-acid propyl, butyl acrylate, a methyl methacrylate, ethyl methacrylate, methacrylic-acid propyl, methacrylic-acid butyl, etc. are used especially preferably.

[0052] As other vinyl system monomers used for this invention An acrylic acid and its alpha-, or beta-alkyl derivatives, such as alpha-ethyl acrylic acid and a crotonic acid; A fumaric acid, Partial saturation dicarboxylic acid, its monoester derivative, and diester derivatives, such as a maleic acid, a citraconic acid, and an itaconic acid; Succinic-acid MONOAKURIRURO yloxy ethyl ester, Succinic-acid mono-methacryloiloxy-ethyl ester, fumaric-acid mono-acryloyloxyethyl ester fumaric-acid mono-methacryloiloxy-ethyl ester, acrylonitrile, a methacrylonitrile, acrylamide, etc. can be mentioned.

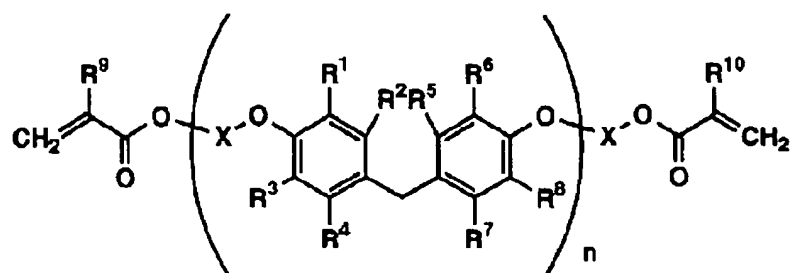
[0053] The ion structure of cross linkage may be introduced into the above-mentioned vinyl system binding resin. In ion bridge formation installation, the ion structure of cross linkage is formed of the coordinate bond (ionic bond) of the carboxyl group of vinyl system binding resin, and a metal ion that what is necessary is just to make polyvalent metal react. Here, as a desirable polyvalent metal compound, the acetate of alkaline earth metal and a zinc group metal, an oxide, etc. can be mentioned, for example.

[0054] Moreover, it is desirable to use the cross linking agent expressed with the following general formula (c) in this invention.

[0055]

[Formula 5]

一般式(c)



[0056] In a general formula (c), R¹-R⁸ express the alkyl group which is not permuted [the permutation of a hydrogen atom, a halogen atom, and carbon numbers 1-10, and], a cycloalkyl radical, or an aryl group. R⁹ and R¹⁰ express the shape of a hydrogen atom or a chain of carbon numbers 1-6, and an annular alkyl group. X expresses the shape of the alkylene group of the shape of a chain of carbon numbers 1-6, a polymethylene radical, and a chain of carbon numbers 2-6, an annular alkylidene radical, or a mere joint hand. n is the number of 1-5.

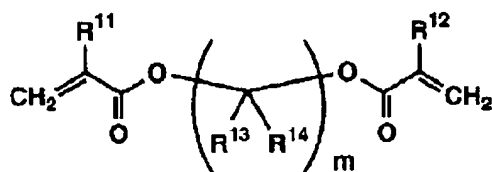
[0057] It will soft-segment-ize too much that n is six or more in the cross linking agent expressed with a general formula (c), and sufficient mechanical strength will no longer be obtained.

[0058] Moreover, it is also desirable to use the cross linking agent expressed with the following general formula (d) in this invention.

[0059]

[Formula 6]

一般式(d)



[0060] In a general formula (d), R¹¹ and R¹² express the shape of a hydrogen atom and a chain of carbon numbers 1-6, and an annular alkyl group. R¹³ and R¹⁴ express the alkyl group which is not permuted [the permutation of a hydrogen atom and carbon numbers 1-10, and], a cycloalkyl radical, or an aryl group, and even if R¹³ and R¹⁴ are the same, they may differ. Furthermore, R¹³ and R¹⁴ may form the ring which formed association mutually. m is the number of 3-20.

[0061] as sufficient soft segment as m being two or less in the cross linking agent expressed with a general formula (d) -- **** -- it will not become, but brittleness will actualize, it will soft-segment-ize too much that m is 21 or more, and sufficient mechanical strength will no longer be obtained.

[0062] Furthermore, as amount of the above-mentioned cross linking agent used, among a vinyl system binding resinous principle, 0.1 - 10 % of the weight is desirable, and is 0.3 - 6 % of the weight more preferably. If effectiveness sufficient at less than 0.1 % of the weight is not acquired but it exceeds 10 % of the weight, since a degree of cross linking will become high too much, the degree of freedom of resin becomes low at the time of melting, and low-temperature fixable one is spoiled.

[0063] As for said vinyl system binding resin, it is desirable for a coherent point to glass transition point temperature to be 45 degrees C or more. As a synthesis method of this vinyl system binding resin, a suspension polymerization, an emulsion polymerization, solution polymerization, bulk polymerization, etc. can be used.

[0064] Additives, such as a well-known coloring agent and an electrification control agent, can be conventionally added in the toner of this invention, for example, metal chelate color [such as carbon black, the Nigrosine color, and metallized dye,], aniline dye, naphthol yellow, pigment yellow, benzidine yellow, permanent yellow, Permanent Red, brilliant carmine, permanent carmine, and

pyrazolone red, a non-metal copper phthalocyanine blue, a copper phthalocyanine blue, ultra marine blue, other colors, a pigment, or metal oxide powder is used for it.

[0065] Furthermore, the toner of this invention may be made to contain polyolefine. As polyolefine, although the polymer of olefin monomers, such as ethylene, a propylene, a butene, a pentene, a hexene, a heptene, octene, nonene, decene, a 3-methyl-1-butene, a 3-methyl-2-pentene, and a 3-propyl-5-methyl-2-hexene, or the above olefin monomers, and ***** with an acrylic acid, a methacrylic acid, vinyl acetate, etc. correspond, for example, especially polypropylene is desirable.

[0066] The content of these polyolefines has 0.5 - 10 desirable % of the weight in the toner of this invention, and it is more desirable to be blended especially one to 5% of the weight.

[0067] It is in the inclination inferior to fixing properties, such as offset in fixing reinforcement and a heat roll fixing method, at less than 0.5 % of the weight. On the other hand, since it is in the inclination for the fluidity of a toner to be inferior when it exceeds 10 % of the weight, image quality deteriorates by poor developer flow, or it is easy to generate problems, like an ingredient causes stagnation within a toner and the hold container of a developer.

[0068] Furthermore, non-subtlety particles, such as an inorganic oxide of SiO₂ which could also add the plasticizer, for example, carried out hydrophobing of the front face, and TiO₂ grade, and SiC, the metallic soap of zinc stearate, and a well-known thing can be used.

[0069] The toner of this invention is used as a 1 component developer or a two component developer. When using as a two component developer, it is used mixing with a carrier. As these carriers, well-known things, such as magnetic metal-powder carriers, such as a ferrite, brown iron oxide, and nickel, a coat carrier which carried out the coat of these by resin, and a magnetic powder distributed carrier, can be used.

[0070] Next, the heat fixing approach applied suitable for this invention is explained.

[0071] If the above-mentioned heat fixing approach is explained according to drawing 1, it is formed in the metal cylinder 3 interior which consists of iron which covered tetrafluoroethylene and polytetrafluoroethylene-perfluoro alkoxy vinyl ether copolymers on the front face 2, aluminum, etc. from the upper roller 1 which has the source 4 of heating, and the lower roller 5 formed by silicone rubber etc. In detail, it has a linear heater as a source 4 of heating, and the skin temperature of an upper roller 1 is heated at about about 120-200 degrees C. The record material 6 which besides supported the toner image 7 of this invention for between a roller 1 and lower rollers 5 is passed, and thermofusion fixing of the toner image 7 is carried out on record material. When excessive, while the so-called coiling-round phenomenon which the toner welded to the upper roller 1 does not separate from record material, but coils around an upper roller with record material arose, the problem that where of a fixing roller becomes dirty had raised by the offset phenomenon which the toner which some fused toners welded to the upper roller 1, and it welded to this upper roller 1 after the one revolution by the conventional heat roller fixing approach fixes into another part of record material occurring. In the fixing section, between an upper roller 1 and a lower roller 5, apply a pressure, a lower roller 5 is made to deform, and the so-called nip is formed. As nip width of face, it is 1.5-7mm preferably 1-10mm. Fixing linear velocity has desirable 40 mm/sec - 400 mm/sec. When nip width of face is narrow, it becomes impossible to give heat at a toner to homogeneity, and becomes easy to generate the nonuniformity of fixing. On the other hand, when nip width of face is wide, melting of resin is promoted, and it becomes easy to generate an offset phenomenon.

[0072] In the heat fixing approach of this invention, on the front face 2 of an upper roller 1, the ***** silicone oil paint film of this invention is formed, and many purposes of this invention are efficiently attained by the interaction of this paint film and the toner of this invention. The following [it makes formation in the front face 2 of the upper roller 1 of the ***** silicone oil paint film of this invention into an example] is performed for passing.

[0073] Namely, in the front face 2 of the longitudinal direction of an upper roller 1, the pressure welding of the sinking-in roller 8 is carried out, and it is rotating in the direction of an arrow head. This sinking-in roller 8 will infiltrate the ***** silicone oil of this invention beforehand, a ***** silicone oil will be supplied to the front face of an upper roller 1 from the pole small quantity [every] sinking-in

roller 8 on the occasion of fixing according to rotation of an upper roller 1, and the ***** silicone oil paint film of this invention will be formed in the front face 2 of an upper roller 1 as a result.

[0074]

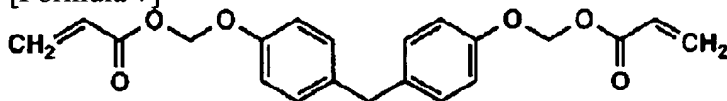
[Example] Although an example explains this invention concretely below, this invention is not limited to these. In addition, all number of copies in the following combination is the weight sections.

[0075] Toluene was put into the separable flask equipped with the preparation thermometer, the stirrer, nitrogen gas installation tubing, and the flowing-down type capacitor of a toner 1** polymer (binder resin), and after introducing nitrogen gas and making the interior into the bottom of an inert atmosphere from gas installation tubing, it heated with the oil bath and was made the ring current temperature of toluene. Subsequently, while the mixture which dissolved the styrene 75 section, the methyl methacrylate 5 section, the n-butyl acrylate 20 section, and the di-t-butyl peroxide 4 section as a polymerization initiator was dropped into the toluene 100 section, solution polymerization was performed, and the amount polymer of macromolecules was obtained.

[0076] Next, solution polymerization was performed while the mixture which dissolved the compound (1) 20 section shown in the toluene 1000 section in the flask which has said amount polymer solution of giant molecules with the styrene 700 section, the methyl methacrylate 150 section, the n-butyl acrylate 150 section, and the following structure expression, and the di-t-butyl peroxide 40 section as a polymerization initiator was dropped. Agitating at the temperature which toluene boils further after dropping termination, it riped for 5 hours and the low-molecular-weight polymer was obtained. Then, desolventization of the toluene was carried out under reduced pressure, raising the temperature of a system gradually to 180 degrees C, it cooled and ground further and target resin A was obtained.

[0077]

[Formula 7]



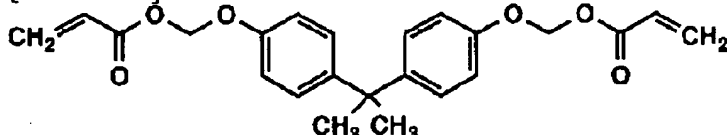
[0078] ** : the preparation aforementioned resin A and the Magenta pigment "C. I. pigment red 122" of a pigment masterbatch were mixed at a rate that a weight ratio is set to 6:4, Flushing processing was performed, and the pigment masterbatch was prepared.

[0079] ** : the manufacture aforementioned resin A 100 section of a toner, the pigment masterbatch 20 section prepared by the above-mentioned **, and the 3 and zinc salt of 5-di-tertiary-butyl salicylic acid 3 section were mixed with the Henschel mixer, and subsequently, after having carried out melting kneading, carrying out cooling solidification and carrying out crushing by the biaxial mold extruder, the coloring particle with a volume mean particle diameter of 8.5 micrometers was obtained using the fines primary crusher and air-current type classifier of a particle collision mold. To the 100 sections of the obtained coloring particle, the hydrophobic silica "R-972" (product made from Japanese Aerosil) 0.5 section and the hydrophobic titania "T-805" (product made from Japanese Aerosil) 1.0 section were added, and the toner (T1) of this invention was manufactured by carrying out mixed processing using a Henschel mixer.

[0080] In toner 2 toner 1, others produced the toner (T2) similarly except for having made the resin presentation of a low-molecular-weight polymer into the styrene 350 section, the acrylic-acid n-butyl 100 section, the methyl-methacrylate 50 section, and the compound (2) 15 section shown with the following structure expression.

[0081]

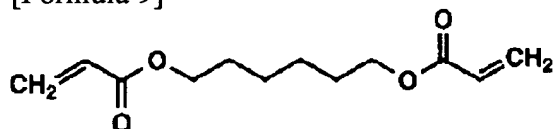
[Formula 8]



[0082] In toner 3 toner 1, others produced the toner (T3) similarly except for having made the resin presentation of a low-molecular-weight polymer into the styrene 700 section, the acrylic-acid n-butyl 150 section, the methyl-methacrylate 150 section, and the compound (3) 20 section shown with the following structure expression.

[0083]

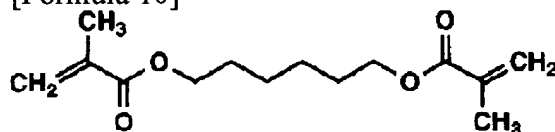
[Formula 9]



[0084] In toner 4 toner 1, others created the toner (T four) similarly except for having made the resin configuration of a low-molecular-weight polymer into the styrene 380 section, the acrylic-acid n-butyl 230 section, the methyl-methacrylate 50 section, and the compound (4) 15 section shown with the following structure expression.

[0085]

[Formula 10]



[0086] In toner 1 toner 1 for a comparison, others produced the toner (H1) similarly except for having made the resin presentation of a low-molecular-weight polymer into the styrene 1400 section, the methylmetaacrylate 300 section, and the n-butyl acrylate 350 section.

[0087] In toner 2 toner 1 for a comparison, others produced the toner (H2) similarly except for having made the resin presentation of a low-molecular-weight polymer into the styrene 250 section, the methylmetaacrylate 50 section, and the n-butyl acrylate 50 section.

[0088] In toner 3 toner 1 for a comparison, the resin presentation of a low-molecular-weight polymer was made into the styrene 1300 section, the methylmetaacrylate 350 section, and the n-butyl acrylate 350 section, and others produced the toner (H3) similarly except for not using a compound (1).

[0089] In toner 4 toner 1 for a comparison, the resin presentation of a low-molecular-weight polymer was made into the styrene 300 section, the methylmetaacrylate 75 section, and the n-butyl acrylate 75 section, and others produced the toner (H4) similarly except for not using a compound (1).

[0090]

[Table 1]

	SLp/SHp	160°C		180°C	
		G' 160 (dyn/cm ²)	G'' 160 (dyn/cm ²)	G' 180 (dyn/cm ²)	G'' 180 (dyn/cm ²)
T 1	14	550	1700	350	870
T 2	8	970	2900	580	1500
T 3	14	600	1900	400	950
T 4	8	1000	2900	600	1750
H 1	18	370	770	290	700
H 2	4	2100	3400	1100	2340
H 3	18	490	1480	280	710
H 4	3	1440	3550	1200	2400

[0091] <Manufacture of a carrier> On the core particle front face of a Cu-Fe system whose volume mean particle diameter is 45 micrometers and whose specific gravity is 5.0, at a rate which becomes 2.0 % of the weight to this core particle, the resin enveloping layer which consists of styrene-methylmethacrylate resin (4/6 (mole ratio)) was made to form, and the resin covering carrier was prepared.

[0092] <Preparation of a developer> Developers 1-4 and the comparison developers 1-4 were prepared by mixing each of the above-mentioned toner (T1 - T four, and H1-H4), and the above-mentioned resin covering carrier using a V shaped rotary mixer so that toner concentration may become 7%.

[0093] <Evaluation conditions> On-the-spot photo evaluation was performed in the example, using a Konica-9028 reconstruction machine as image formation equipment. The point converting [main] and the main conditions of equipment are as follows.

[0094] Photo conductor surface potential = -550VDC bias = -250VAC bias =****-p:-50 - -450VDsd = in addition, 300 micrometers was performed by forming a fixing image about the fixing engine performance using the full colour copying machine "DC-9028" (Konica Corp. make) which converted the configuration of an anchorage device as shown in drawing 1 , and was converted so that a vertical roller might have an LTV rubber layer.

[0095] In addition, as fixing conditions, it considered as process speed 140 mm/sec.

[0096] In addition, it was used, having equipped with the pad which sank in the fluorine system silicone oil as a cleaning device of an anchorage device. These are set to R-1, R-2, and R-3 using an instantiation compound (7), (8), and (13).

[0097] Moreover, the skin temperature of an anchorage device used what can carry out adjustable (120-200 degrees C).

[0098] What, on the other hand, used for the above-mentioned equipment the silicone oil (dimethyl silicone oil) which consists of dimethylpolysiloxane as an anchorage device for a comparison, and the thing using the fluorine system silicone oil (FS-1265: Dow Corning make) whose alkyl fluoride of a side chain is mere trifluoromethyl were used. Let the thing [anchorage device / dimethyl silicone oil use hot calender roll] using the R-ratio 1 and a fluorine system silicone oil be the R-ratio 2.

[0099] <Evaluation> The following evaluations were performed in the obtained toner. The result was shown in Table 2.

[0100] With the developer which used the toner of this invention, the test created the transparency image (OHP image) on OHP by the above-mentioned image formation approach (fixing temperature is 170 degrees C), and evaluated it by the approach shown below. In addition, toner coating weight was evaluated in 0.7×0.05 (mg/cm²).

[0101] Transparency: The following approach estimated the transparency of an OHP image.

[0102] By making into a reference the sheet for OHP with which the toner is not supported by "330 Mold recording spectrophotometer" by Hitachi, the visible spectral transmittance of an image was measured, and it asked for the spectral transmittance in 570nm, and considered as the scale of the transparency of an OHP image.

[0103]

[Table 2]

	オフセット発生温度 (°C) / OHP透過性 (%)				
	R-1	R-2	R-3	R-比1	R-比2
T 1	200/57	200/59	200/60	190/53	180/50
T 2	200/45	200以上/45	200以上/45	190/40	180/36
T 3	200以上/56	200以上/56	200以上/58	180/51	170/43
T 4	200以上/40	200以上/41	200以上/42	190/36	180/27
H 1	180/40	190/40	200/41	170/34	160/24
H 2	190/35	190/36	190/38	170/31	170/20
H 3	190/38	200/31	200/31	160/30	160/21
H 4	190/31	200/31	200/31	160/21	160/19

[0104]

[Effect of the Invention] As the example proved, the heat fixing approach using the toner for electrostatic-charge development by this invention has the effectiveness which offset-proof nature was good, and was good, and was excellent. [of OHP permeability]

[Translation done.]